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(54) **Glass composition, stem and bulb for lamps**

Glaszusammensetzung, Lampenstiel und Birne

Composition du verre, tige et ampoule de lampe

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(73) Proprietor: **MATSUSHITA ELECTRIC INDUSTRIAL
CO., LTD.**
Kadoma-shi, Osaka (JP)

(72) Inventors:
• **Kondoh, Toshifumi**
Takatsuki-shi, Osaka 569-1136 (JP)
• **Koyamada, Yutaka**
Takatsuki-shi, Osaka 569-1022 (JP)
• **Iwama, Katsuaki**
Suita-shi, Osaka 565-0851 (JP)

(74) Representative:
Hafner, Dieter, Dr.rer.nat., Dipl.-Phys.
Dr. Hafner & Stippl,
Patentanwälte,
Schleiermacherstrasse 25
90491 Nürnberg (DE)

(56) References cited:

EP-A- 0 603 933 **DE-A- 3 135 910**

- **PATENT ABSTRACTS OF JAPAN vol. 008, no. 222 (C-246), 9 October 1984 (1984-10-09) - & JP 59 107941 A (NIHON DENKI GLASS KK), 22 June 1984 (1984-06-22)**
- **KUMMEL U: "On the darkening of discharge tubes" APPLIED PHYSICS, JUNE 1975, WEST GERMANY, vol. 7, no. 2, pages 93-97, XP002110323 ISSN: 0340-3793**
- **PATENT ABSTRACTS OF JAPAN vol. 014, no. 189 (P-1037), 17 April 1990 (1990-04-17) & JP 02 033741 A (NEC CORP), 2 February 1990 (1990-02-02)**
- **PATENT ABSTRACTS OF JAPAN vol. 097, no. 005, 30 May 1997 (1997-05-30) & JP 09 012332 A (NIPPON ELECTRIC GLASS CO LTD), 14 January 1997 (1997-01-14)**
- **PATENT ABSTRACTS OF JAPAN vol. 018, no. 357 (C-1221), 6 July 1994 (1994-07-06) & JP 06 092677 A (TOSHIBA GLASS CO LTD), 5 April 1994 (1994-04-05)**

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Description

[0001] The present invention relates to a glass composition for various kinds of lamps such as a fluorescent lamp and an incandescent lamp, and a stem and a bulb for lamps that include the glass composition.

[0002] A glass composition for lamps is roughly divided into two groups. One is for stems including an exhaust tube and a flared base, and the other is for bulbs such as a luminescent bulb. In general, lead glass comprising 4 to 28 wt% of lead has been used for stems because it is handled easily in a forming process while heating. The glass bulb has been formed of a soda-lime silicate glass comprising 10 to 20 wt% of sodium oxide or about the same lead glass as for stems.

[0003] For environmental protection, cutting back on environmentally harmful materials is desired. In the field of lighting, problematic contaminants are lead and mercury. Lead is included in the glass for stems and bulbs. Therefore, some lead-free glass compositions have been proposed.

[0004] Tokkai-Hei 6-206737 discloses a glass composition free of PbO as well as toxic F, Sb₂O₃ and As₂O₃. The glass composition disclosed specifically, expressed in wt%, is e.g. SiO₂: 68.0, Al₂O₃: 3.4, Li₂O: 1.2, Na₂O: 7.4, K₂O: 5.0, BaO: 8.7, SrO: 2.9, MgO: 1.3, CaO: 1.9 and SO₂: 0.1.

[0005] Tokkai-Hei 9-12332 also discloses a glass composition free of PbO. In the glass composition, BaO is reduced because BaO tends to cause opacity of glass for stems, especially when used in a Danner method. The glass composition contains 0.3 to 3.5 wt% of BaO, and alkali metal oxides R₂O (R = Li, Na, K) than alkaline earth metal oxides R'O (R' = Mg, Ca, Sr, Ba) so as to keep shape-formability. The glass compositions disclosed specifically contains 15.5 to 16.0 wt% of R₂O.

[0006] Tokkai-Hei 6-92677 also discloses a glass composition free of PbO. In the glass composition, TiO₂ and CeO₂ improve the solarization-resistant property and Fe₂O₃ increases the absorption of ultraviolet rays. In this glass composition, a predetermined amount of alkali metal oxide is considered necessary so as to suppress a rise of the softening point of the glass. The glass composition disclosed specifically contains at least about 15 wt% of R₂O.

[0007] The glass compositions as described above can truly provide lead-free glass for lamps, but are not designed to reduce another environmentally affective material, mercury. At the present time, mercury is sealed into fluorescent lamps in more than a theoretically necessary amount for lighting because there is a necessity to consider the consumption of mercury by the glass while lighting.

[0008] Therefore, it is an object of the present invention to provide a glass composition for lamps that is substantially free of lead and can reduce mercury consumption, and a stem and a bulb for lamps that can meet the need of environmental protection.

[0009] One embodiment of the glass composition for lamps of the present invention is defined in claim 1.

[0010] The glass composition provides glass for lamps that is substantially free of lead and has an advantage of suppressing the consumption of mercury in the lamps. In lighting, alkali ions such as sodium ions in the glass tend to diffuse, especially to move toward the inside of the bulb. Moving alkali ions facilitate the reaction of the alkali ions with mercury vapor and the fixation of mercury into the voids of the alkali ions. Mercury trapped in the voids no longer contributes to the electric discharge of the lamp. The glass composition of the present invention contains less R₂O (R = Li, Na, K) than conventional glass compositions. In addition, the glass composition contains diffusion inhibitors for alkali ions, e.g. BaO, in such an extent that the glass can be smoothly formed into a predetermined shape. Therefore, the glass composition can reduce the consumption of mercury.

[0011] Another embodiment of the glass composition for lamps of the present invention is defined in claim 2.

[0012] The glass composition also provides glass for lamps that is substantially free of lead and has an advantage of suppressing the consumption of mercury in the lamps. In particular, sodium oxide, which is considered to easily form an amalgam with mercury, is included in not more than 7 wt%. In this composition, the total amount of Na₂O, K₂O and Li₂O is preferably not more than 13 wt%.

[0013] In one embodiment of the glass composition of the present invention, the total amount of Na₂O, K₂O and Li₂O is preferably not more than the total amount of MgO, CaO, SrO and BaO.

[0014] The glass composition of the present invention is preferable in terms of environmental protection. The glass composition is determined by taking shape-formability in heating and other properties into consideration.

[0015] An embodiment of the stem and the bulb of the present invention includes glass having the glass composition of the present invention as described above. Thus, lamps that can meet the need of environmental protection are provided.

[0016] Figure 1 is a longitudinal-sectional view of a fluorescent lamp including a bulb and stems having a glass composition of the present invention.

[0017] An embodiment of the glass composition includes SiO₂, Al₂O₃, Na₂O, K₂O, MgO, CaO, SrO and BaO as indispensable constituents and Li₂O, B₂O₃, Sb₂O₃, Fe₂O₃, TiO₂ and CeO₂ as dispensable constituents. Hereinafter, these constituents will be described.

[0018] SiO₂ is an essential component for formation of the glass. When SiO₂ is contained in an amount of less than

65wt%, the expansion coefficient becomes excessively high and chemical resistance deteriorates. When it exceeds 75wt%, the expansion coefficient becomes excessively low, and shape forming becomes difficult because of its excessively high softening point.

[0019] An Al_2O_3 content less than 0.5wt% degrades the chemical resistance, and an Al_2O_3 content more than 4wt% results in an inhomogeneous glass and more striae.

[0020] Na_2O and K_2O , alkali metal oxides, are used to reduce the viscosity of the glass and improve the shape-forming property in heating. When the two oxides are included in the range as described above, a sufficiently high electrical resistance can be obtained due to the mixed alkali effect. However, an excess amount of the alkali metal oxides, especially Na_2O , makes it difficult to reduce the consumption of mercury. Viewed in this light, each content of Na_2O and K_2O is preferably 1 to 7 wt%.

[0021] MgO and CaO , alkaline-earth metal oxides, improve the electric insulation and the chemical resistance. However, a MgO content of less than 0.5wt% or a CaO content of less than 1wt% fails to provide these advantages. A MgO content of more than 5wt% or a CaO content of more than 8wt% is not preferable because the glass may become opaque.

[0022] SrO improves the hardness and the chemical resistance of the glass. However, a SrO content of less than 1wt% fails to provide these advantages. A SrO content of more than 7wt% increases the opacity. The SrO content is preferably in the range from 2.5 to 7wt%. BaO serves to lower the softening point and raise the electric resistance. A BaO content of less than 3.5wt% fails to provide this advantage. A BaO content of more than 7wt% increases the opacity. The BaO content is preferably in the range from 4 to 6.5wt%. SrO and BaO are excellent diffusion inhibitors of alkali ions.

[0023] A Li_2O content not more than 2wt% is preferable. Li_2O is superior to Na_2O and K_2O in reducing the viscosity of glass and improving a shape-forming property. Li_2O enhances the mixed alkali effect. However, an excess amount of Li_2O causes an overly high expansion coefficient.

[0024] A B_2O_3 content not more than 3wt% is preferable. B_2O_3 increases the strength and the durability of the glass, and reduces the opacity. A B_2O_3 content of more than 3wt% is not preferable because the expansion coefficient becomes too small.

[0025] A Sb_2O_3 content not more than 1wt% is preferable. Sb_2O_3 works as a clarifier of the glass. A Sb_2O_3 content of more than 2wt% is not preferable because re-foaming or blackening may occur during a heating process.

[0026] A Fe_2O_3 content not more than 0.2wt% is preferable. Fe_2O_3 has a property of absorbing ultraviolet rays, and serves to suppress the radiation of ultraviolet rays from the fluorescent lamp. A Fe_2O_3 content of more than 0.2wt% is not preferable because the light transmissivity in a visible range of the glass drops to lower a luminous flux of the lamp.

[0027] A TiO_2 content and a CeO_2 content not more than 1wt% are preferable. These constituents suppress the solarization of the glass caused by ultraviolet rays. Adding more than 1wt% of the constituents hardly enhances the solarization-resistance.

[0028] The total amount of the alkali oxides R_2O is preferably not more than the total amount of the alkaline earth metal oxides $\text{R}'\text{O}$ that suppress the diffusion of the alkali metal, because mercury consumption can be reduced more effectively.

[0029] A preferable glass composition as described above does not contain lead, but has the same shape-formability in heating as conventional lead glass compositions. Therefore, by the previously known methods, various kinds of stems and bulbs for lamps such as an arc tube for mercury vapor-filled discharge lamps can be formed with the glass.

[0030] A straight tube fluorescent lamp shown in Fig. 1 is an embodiment of the lamps including the glass composition of the present invention. As shown in Fig. 1, stems (flared stems) 2 are attached to both of the ends of a glass bulb 1 so as to seal it. A pair of lead wires 3 goes through each of the stems 2 while keeping the airtightness in the glass bulb. A filament coil 4 coated with an emissive substance is laid so as to connect the end portions of the lead wires 3. Bases 5 are fixed in the ends of the glass bulb 1, and base pins 6 in connection with the lead wires 3 are attached to the base 5. A fluorescent-substance layer 7 is formed on the inside surface of the glass bulb 1, and a predetermined amount of mercury and rare gas such as argon is sealed in the glass bulb 1.

[0031] Hereinafter, the present invention will be described by way of examples.

[0032] Table 1 shows glass composition Examples of the present invention and glass composition Comparative Examples. A glass composition in Comparative Example 1 is an example of soda-lime glass used for bulbs of fluorescent lamps. Comparative Example 2 shows an example of lead glass used mainly for stems of lamps.

[0033] Raw materials prepared so as to have each composition in Table 1 were melted in platinum crucibles in an electric furnace. The melting material was spread on a carbon plate to obtain glass samples, followed by annealing them.

Table 1

		Example							Comparative Example	
		1	2	3	4	5	6	7	1	2
Glass composition wt%	SiO ₂	70.0	68.0	72.0	69.0	70.0	70.5	71.0	72.0	58.5
	Al ₂ O ₃	2.0	1.5	1.0	3.5	2.5	2.5	1.5	1.7	1.0
	Na ₂ O	7.0	5.0	4.0	6.0	4.0	3.0	5.5	16.4	8.3
	K ₂ O	6.0	7.0	5.0	2.0	6.0	7.0	4.0	1.1	4.0
	MgO	1.5	2.0	1.0	3.0	4.0	3.0	1.0	2.7	
	CaO	2.0	4.5	2.5	6.0	3.0	1.5	3.0	5.6	
	SrO	6.0	5.0	7.0	2.5	4.0	4.0	6.0		
	BaO	5.5	6.0	4.0	6.5	5.0	6.5	6.0		0.5
	Li ₂ O		1.0	1.5		1.4	0.5			
	B ₂ O ₃			2.0	1.0		1.0	1.0		
	Sb ₂ O ₃				0.5			0.5	0.5	0.2
	Fe ₂ O ₃					0.1				
	TiO ₂						0.5			
	CeO ₂							0.5		
	PbO									27.5
Linear Expansion Coefficient [$\times 10^{-7} / ^\circ\text{C}$]		94.5	94.8	94.0	93.5	95.0	94.0	94.0	99.0	94.0
Softening Point [$^\circ\text{C}$]		680	665	685	670	675	685	680	690	615
Operation Temperature [$^\circ\text{C}$]		990	985	995	990	995	990	985	1005	955
Eluted Amount of Alkali [mg]		0.4	0.3	0.4	0.5	0.4	0.3	0.5	0.8	0.7

[0034] The linear expansion coefficient is an average expansion coefficient between 0 to 300 °C, and a value obtained by a measurement according to "a test method for the average expansion coefficient of glass" in Japanese Industrial Standards R 3102. The softening point is a value obtained by a measurement according to "a test method for the softening point of glass" in Japanese Industrial Standards R 3104. The operation temperature is a temperature corresponding to a viscosity of 10³Pa •s, which is determined from a viscosity curve measured at a high temperature. The eluted amount of alkali is a value obtained by a measurement according to Japanese Industrial Standards R 3502.

[0035] As shown in Table 1, the glass compositions in the examples have sufficient properties to use them for glass for lamps, especially for stems and bulbs. With the glass composition of Examples 1 to 7, stems (100 pieces per composition) for a 40W straight-tube fluorescent lamp were formed. The glass compositions did not cause any problems in shape-forming, and the glass strength and the sealing property with lead wires of a dumet (Dumet wires) also were satisfactory.

[0036] With stems and bulbs having the glass composition of Examples 1, 4 and 7 and Comparative Example 1, 50 pieces of 40 W straight-tube fluorescent lamps were prepared. The glass compositions caused no problems in manufacturing.

[0037] Initial luminous flux, its maintaining ratio and a mercury consumption amount were measured. For the measurement, five lamps per glass composition were used.

Table 2

		Example			Com. Example
		1	4	7	1
Initial Luminous Flux [lm]		3480	3480	3460	3450
Life test (1000 hrs)	Luminous Flux Maintaining Ratio [%]	97.0	97.0	97.5	96.0
	Mercury Consumption Amount [mg]	0.4	0.5	0.5	0.7

[0038] The luminous flux maintaining ratio in Table 2 refers to a ratio of a luminous flux at the point after 1000 hours of life test to a luminous flux at the point after 100 hours of life test.

[0039] The mercury consumption amount is measured in a chamber with a heater, an evacuator and a quadrupole mass spectrometer. In this chamber, after breaking a lamp, the chamber is evacuated at 40°C until no mercury is detected. Then, the chamber is heated and kept at 450°C until no mercury is detected. The mercury consumption amount is calculated based on the total amount of mercury detected from the chamber.

[0040] As seen in Table 2, the mercury consumption amounts in the lamps of Examples 1, 4 and 7 of the present invention are less than the amount in the conventional lamp of Comparative Example 1. In addition, the lamps of the Examples have performance higher than the conventional lamps in the initial luminous flux and the luminous maintaining ratio.

[0041] Basically, the glass composition is free of lead, and has a good shape-formability in heating and chemical resistance enough to use for lamps, so the glass composition can be utilized for other lamps such as a light bulb, not to mention other types of fluorescent lamps such as a compact-type fluorescent lamp.

Claims

1. A glass composition for glass lamps consisting essentially of, expressed in percentages by weight:

SiO ₂	65-75,
Al ₂ O ₃	0.5-4,
Na ₂ O	1-8,
K ₂ O	1-8,
Li ₂ O	0-2,
MgO	0.5-5,
CaO	1-8,
SrO	1-7,
BaO	3.5-7,
B ₂ O ₃	0-3,
Sb ₂ O ₃	0-1,
Fe ₂ O ₃	0-0.2,
TiO ₂	0-1,
CeO ₂	0-1;

characterized in that the total amount of Na₂O, K₂O and Li₂O is not more than 13 weight %, and the total amount of Na₂O, K₂O and Li₂O is less than the total amount of MgO, CaO, SrO and BaO.

2. A glass composition for glass lamps consisting essentially of, expressed in percentages by weight:

SiO ₂	65-75,
Al ₂ O ₃	0.5-4,
Na ₂ O	1-7,
K ₂ O	1-8,
Li ₂ O	0-2,
MgO	0.5-5,

(continued)

CaO	1-8,
SrO	1-7,
BaO	4-6.5,
B ₂ O ₃	0-3,
Sb ₂ O ₃	0-1,
Fe ₂ O ₃	0-0.2,
TiO ₂	0-1,
CeO ₂	0-1.

characterized in that the total amount of Na₂O, K₂O and Li₂O is not more than 13 weight %, and the total amount of Na₂O, K₂O and Li₂O is not more than the total amount of MgO, CaO, SrO and BaO.

3. A stem for lamps including glass which has a glass composition as claimed in claim 1 or 2.
4. A bulb for lamps including glass which has a glass composition as claimed in claim 1 or 2.

Patentansprüche

1. Glaszusammensetzung für Glaslampen, im wesentlichen bestehend aus (in Gewichtsprozent):

SiO ₂	65-75,
Al ₂ O ₃	0,5-4,
Na ₂ O	1-8,
K ₂ O	1-8,
Li ₂ O	0-2,
MgO	0,5-5,
CaO	1-8,
SrO	1-7,
BaO	3,5-7,
B ₂ O ₃	0-3,
Sb ₂ O ₃	0-1,
Fe ₂ O ₃	0-0,2,
TiO ₂	0-1,
CeO ₂	0-1;

dadurch gekennzeichnet, daß die Gesamtmenge an Na₂O, K₂O und Li₂O höchstens 13 Gew.-% beträgt und die Gesamtmenge an Na₂O, K₂O und Li₂O kleiner als die Gesamtmenge an MgO, CaO, SrO und BaO ist.

2. Glaszusammensetzung für Glaslampen, im wesentlichen bestehend aus (in Gewichtsprozent):

SiO ₂	65-75,
Al ₂ O ₃	0,5-4,
Na ₂ O	1-7,
K ₂ O	1-8,
Li ₂ O	0-2,
MgO	0,5-5,
CaO	1-8,
SrO	1-7,
BaO	4-6,5,
B ₂ O ₃	0-3,
Sb ₂ O ₃	0-1,

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(fortgesetzt)

Fe ₂ O ₃	0-0,2,
TiO ₂	0-1,
CeO ₂	0-1;

dadurch gekennzeichnet, daß die Gesamtmenge an Na₂O, K₂O und Li₂O höchstens 13 Gew.-% beträgt und die Gesamtmenge an Na₂O, K₂O und Li₂O nicht größer als die Gesamtmenge an MgO, CaO, SrO und BaO ist.

3. Fuß für Lampen, enthaltend Glas mit einer Glaszusammensetzung nach Anspruch 1 oder 2.
4. Kolben für Lampen, enthaltend Glas mit einer Glaszusammensetzung nach Anspruch 1 oder 2.

Revendications

1. Composition de verre pour lampes en verre essentiellement constituée de, exprimée en pourcentages en poids :

SiO ₂	65 à 75,
Al ₂ O ₃	0,5 à 4,
Na ₂ O	1 à 8,
K ₂ O	1 à 8,
Li ₂ O	0 à 2,
MgO	0,5 à 5,
CaO	1 à 8,
SrO	1 à 7,
BaO	3,5 à 7,
B ₂ O ₃	0 à 3,
Sb ₂ O ₃	0 à 1,
Fe ₂ O ₃	0 à 0,2,
TiO ₂	0 à 1,
CeO ₂	0 à 1 ;

caractérisée en ce que la quantité totale de Na₂O, K₂O et Li₂O ne dépasse pas 13 % en poids, et la quantité totale de Na₂O, K₂O et Li₂O est inférieure à la quantité totale de MgO, CaO, SrO et BaO.

2. Composition de verre pour lampes en verre essentiellement constituée de, exprimée en pourcentages en poids :

SiO ₂	65 à 75,
Al ₂ O ₃	0,5 à 4,
Na ₂ O	1 à 7,
K ₂ O	1 à 8,
Li ₂ O	0 à 2,
MgO	0,5 à 5,
CaO	1 à 8,
SrO	1 à 7,
BaO	4 à 6,5,
B ₂ O ₃	0 à 3,
Sb ₂ O ₃	0 à 1,
Fe ₂ O ₃	0 à 0,2,
TiO ₂	0 à 1,
CeO ₂	0 à 1 ;

caractérisée en ce que la quantité totale de Na₂O, K₂O et Li₂O ne dépasse pas 13 % en poids, et la quantité

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totale de Na_2O , K_2O et Li_2O ne dépasse pas la quantité totale de MgO , CaO , SrO et BaO .

3. Pied pour lampes comprenant du verre qui présente la composition de verre selon la revendication 1 ou 2.

5 4. Ampoule pour lampes comprenant du verre qui présente la composition de verre selon la revendication 1 ou 2.

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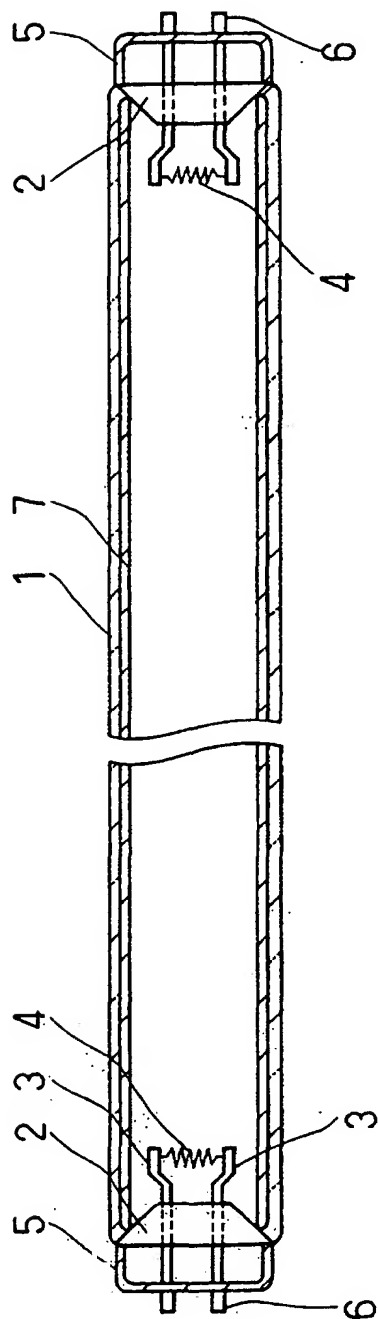


FIG.1